

Use of the Semi-Quantitative Calibration Mode for Rapid Sample Screening

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Key Words

- ELEMENT 2
- High Resolution ICP-MS
- Rapid Sample Screening
- Semi Quantitative Analysis

Introduction

In routine analytical laboratories there is frequently a need for rapid, multi-element analyses as a preliminary examination of unknown samples. This wide-range, multi-element screening is made to determine which elements can be detected in the sample by the specified technique and their approximate concentrations. Such measurements are performed in an analysis mode termed 'semi-quantitative' as it is not designed to deliver the ultimate accuracy but to provide results of sufficient accuracy in both an analysis time and labour efficient manner. For subsequent accurate, quantitative analysis this initial screening helps to:

- determine the appropriate dilution required (e.g. for analytes that, without dilution, may be over the analytical range of the instrument)
- identify sources of potentially interfering matrix-induced spectral interferences to subsequently define the instrument settings (resolution etc.) for the target analytes
- define the relevant concentration ranges for calibration standards as well as appropriate internal standard elements and concentrations
- control and evaluate potential blank contribution from the acids, solvents and water used in the sample preparation process.

In the semi-quantitative approach implemented in the ELEMENT software, concentrations in unknown samples are calculated from isotope intensities using a 'response curve' of mass against isotopic sensitivity. This response curve is dependent on the relatively uniform element to element sensitivity of the Thermo Scientific ELEMENT 2, such that a response curve may be determined from the analysis of a standard containing only a selection of isotopes across the mass range - it is not necessary to include every target isotope. Once this curve has been generated, unknown samples may be analysed and elemental concentrations calculated directly from this curve.

Each instrument is delivered with such a default response curve. The use of this default calibration, when used with internal standardization, provides acceptable accuracy for the majority of elements, although less accurate data for elements with a high ionisation potential may initially be obtained.

The aim of this Application Note is to describe how the initial accuracy of semi-quantitative analyses with the ELEMENT 2 can be improved. Its suitability as a routine, rapid, multi-element screening of unknown samples is evaluated from the results obtained for a selection of water Certified Reference Materials (CRMs).

Methodology

The first step to improving the accuracy of semi-quantitative analyses with the Thermo Scientific ELEMENT 2 is to generate a new response curve of mass against isotopic sensitivity replacing the existing default file ('default.rsp'). As the response curve is instrument specific and depends on both operating conditions and measurement parameters used, regular adjustment of the absolute count rates of the response curve is recommended. A series of response files may be generated, e.g. for different sample introduction systems or different sample types.

In order to obtain the most accurate full mass range response curve, a standard containing as many elements as possible should be used to initially define it. Commercially available multi-element standards (described as being for either AAS or for ICP-OES/MS with wide elemental coverage) may be combined into a single solution and diluted to 50 µg l⁻¹ for this analysis. The actual concentration used may vary depending on the analytical task but the use of sub-µg l⁻¹ concentrations should be avoided due to elemental stability/contamination issues. There are certain problems with inter-element compatibility and/or stability of mixed standards at lower concentrations, but in our experience standards at this concentration were found to be stable for at least 3 hours: more than sufficient time to perform this initial recalibration of the response curve.

Software Required

- The ELEMENT method file (a '*.met' file that determines the analysis parameters for each target isotope) for the definition of the response curve should then be created using the Method Editor. Isotopes for all elements in the calibration solution that are free from isobaric interferences should be included. As a first approximation, the choice of isotope and associated measurement parameters (samples per peak, acquisition and integration windows, etc) for a given resolution should match as closely as possible those used for the actual screening method. For example, as high resolution (R=10000) is usually required for the determination of As, Ge, K and Se in many samples, only isotopes of these elements (plus the chosen internal standards) should be used to generate the high resolution mass response curve. The use of similar scan parameters in the two methods enables the synchronization of the magnet jumps, thus compensating for any variations in response caused by the changes in the accelerating voltage in the EScan analysis mode.
- The ELEMENT Concentration file (*.std) should be created using the Standard Editor defining the concentrations of the elements in the solution used to define the response curve (50 µg l⁻¹ therefore in the suggested example).
- The Response file (*.rsp) specific to the calculated response curve is automatically created after the analysis of the calibration solution as a 'Standard' analysis type in a Sequence. The Analysis Parameters for this Standard should contain the appropriate *.met, *.std, and *.rsp files and its 'Quantification Type' should be set as 'Update Response Table (SEMIQUANT)'.

From this point, the newly created response file (*.rsp) contains new responses for the calibrated elements. The relatively time-consuming (approximately 1 hour including method setup and preparation of standards) calibration procedure described above only needs to be repeated after major changes in the Thermo Scientific ELEMENT 2's sample introduction system (e.g. replacement of the standard nebulizer with a desolvating one) or in operating conditions (i.e. use of 'cold' plasma or laser ablation) which may result in changes in ionization efficiency.

Of course, the response curve is dependent on the sensitivity of all elements used to generate it and is therefore subject to daily variations depending on the 'status' of the instrument: e.g. conditions of the cones, torch, etc. In practise however, these daily variations can be corrected for by:

- (I) using internal standardization
- (II) rapid minor adjustment of the response curve

The latter can be performed on daily/weekly basis through the analysis of a standard solution containing only a few of the elements used to define the initial response curve.

At Analytica AB, the elements used in this minor update analysis are Li, Al, Mn, In, Ba, Tl in low resolution mode, Al, Sc, Mn, In, Ba, Tl in medium resolution mode and K, As, In in high resolution mode. It is important to note that elements without severe memory effects are used in this standard. The minor adjustment procedure requires less than 10 min to complete and is performed in the same way as described above. The selection of the internal standards and their concentrations is highly dependent on analytical task, sample matrix and accuracy required. As a rule, for the purity testing of water and reagents only In used as internal standard in our laboratory, while a mixture of Sc, In and Tl is preferable for 'real-life' samples.

- The Analysis Parameters for the unknown samples require the selection of 'Quantification (SEMIQUANT)' in the 'Quantification Type', the same *.rsp response file as previously generated and selection of the appropriate *.std Internal Standard file.

Results

In order to assess the accuracy of this semiquantitative quantification for multi-elemental screening, four water CRMs were analysed in triplicate in an analytical sequence. The CRMs used were:

- HPS Trace Metals in Drinking Water (High-Purity Standards, USA)
- NIST SRM 1640, Trace Elements in Natural Water (NIST, USA)
- SLEW-2, Estuarine Water CRM for Trace Metals (NRC, Canada)
- SLRS-4, River Water CRM for Trace Metals (NRC, Canada).

The first two CRMs were analysed after a 10-fold dilution and the final two after a 4-fold dilution. An internal standard solution containing Sc, In and Tl was added to all samples and blanks. No mathematical corrections for isobaric overlaps (e.g. from Sn on Cd) and spectral interferences (e.g. from BaO on Eu) were performed, though such option is now available in the latest release of the ELEMENT software. Semi-quantitative results for these samples are shown in Table 1 along with certified, recommended or previously reported concentrations. Although approximately 70 elements were monitored, only results for elements presented at detectable concentrations are given.

The accuracy of the semi-quantitative analysis is evident from a comparison of the results obtained with the target concentrations. The agreement is generally very good for the majority of the elements in the HPS, SRM 1640 and SLRS-4 CRMs. Slightly lower analyte recoveries in SLEW-2 are probably caused by matrix effects from the sample matrix (estuarine water) that are not adequately corrected for by the set of internal standards used.

ELEMENT (RESOLUTION)	UNIT	HPS FOUND	HPS CERTIFIED	SRM 1640 FOUND	SRM 1640 CERTIFIED	SLRS-4 FOUND	SLRS-4 CERTIFIED	SLEW-2 FOUND	SLEW-2 CERTIFIED
Ag (Low)	ng l ⁻¹	2010±20	2000	7460±130	7620±250	1.4±0.2	NA	4.7±1.3	NA
Al (Low)	µg l ⁻¹	116±2	120	48.7±2.2	52.0±1.5	53.5±1.2	54±4	1.45±0.19	1.96*
As (High)	µg l ⁻¹	79.5±1.6	80	27.6±0.7	26.67±0.41	0.58±0.04	0.68±0.06	0.59±0.06	0.792±0.082
B (Low)	µg l ⁻¹	0.28±0.04	NA	302±5	301.1±6.1	4.93±0.03	NA	1080±30	NA
Ba (Low)	µg l ⁻¹	47.8±0.7	50	142±4	148±2	12.7±0.2	12.2±0.6	14.5±0.8	17.0*
Be (Low)	µg l ⁻¹	20.7±0.6	20	35.2±1.1	34.94±0.41	0.006±0.001	0.007±0.002	< 0.004	NA
Bi (Low)	µg l ⁻¹	10.2±0.3	10	< 0.002	NA	0.0013±0.0002	NA	0.0061±0.0004	NA
Ca (Medium)	mg l ⁻¹	26.4±0.8	35	5.2±0.3	7.045±0.089	4.24±0.10	6.2±0.2	95±2	NA
Cd (Low)	µg l ⁻¹	9.83±0.34	10	22.6±0.4	22.79±0.96	0.012±0.001	0.012±0.002	0.025±0.003	0.019±0.002
Ce (Low)	ng l ⁻¹	45±1	NA	351±1	NA	348±7	361*	15.7±1.3	NA
Co (Medium)	µg l ⁻¹	30.3±0.8	30	19.7±0.4	20.28±0.31	0.032±0.002	0.033±0.006	0.046±0.003	0.055±0.008
Cr (Medium)	µg l ⁻¹	21.6±0.4	20	40.5±1.2	38.6±1.6	0.335±0.004	0.33±0.02	0.138±0.011	0.169±0.018
Cs (Low)	ng l ⁻¹	< 1	NA	133±2	NA	5.4±0.3	NA	297±24	NA
Cu (Medium)	µg l ⁻¹	20.8±0.2	20	86.2±0.9	85.2±1.2	1.80±0.14	1.81±0.08	1.28±0.09	1.62±0.11
Dy (Low)	ng l ⁻¹	9.5±1.5	NA	35.6±0.9	NA	23.4±0.3	NA	2.5±0.4	NA
Er (Low)	ng l ⁻¹	< 0.5	NA	16.9±1.2	NA	11.8±0.3	NA	3.3±0.8	NA
Eu (Low)	ng l ⁻¹	7.5±1.5	NA	27.5±1.1	NA	7.5±0.4	NA	1.8±0.3	NA
Fe (Medium)	µg l ⁻¹	98.7±1.8	100	31.8±0.6	34.3±1.6	104±5	103±5	2.08±0.14	2.37±0.37
Ga (Medium)	ng l ⁻¹	< 10	NA	< 10	NA	4.5±0.7	NA	< 4	NA
Gd (Low)	ng l ⁻¹	8.2±1.2	NA	53.8±4.7	NA	34.0±0.2	NA	0.6±0.2	NA
Hf (Low)	ng l ⁻¹	< 2	NA	5.1±0.4	NA	2.8±0.3	NA	< 1	NA
Ho (Low)	ng l ⁻¹	0.8±0.2	NA	6.8±1.4	NA	4.8±0.3	NA	1.6±0.4	NA
K (High)	mg l ⁻¹	2.6±0.2	2.5	1.02±0.05	0.994±0.027	0.640±0.010	0.680±0.020	123±4	NA
La (Low)	ng l ⁻¹	22±1	NA	314±3	NA	270±8	320*	13±2	NA
Li (Low)	µg l ⁻¹	< 0.02	NA	53.0±0.2	50.7±1.4	0.56±0.02	NA	46.8±2.7	NA
Lu (Low)	ng l ⁻¹	0.6±0.1	NA	2.8±0.4	NA	1.8±0.2	NA	0.4±0.1	NA
Mg (Medium)	mg l ⁻¹	8.7±0.3	9	5.73±0.08	5.819±0.056	1.64±0.02	1.6±0.1	320±6	NA
Mn (Medium)	µg l ⁻¹	38.1±2.8	40	116±3	121.5±1.1	3.30±0.04	3.37±0.18	15.6±0.8	17.1±1.1
Mo (Low)	µg l ⁻¹	103±2	100	47.2±1.0	46.8±0.3	0.194±0.009	0.21±0.02	3.48±0.15	3.7
Na (Medium)	mg l ⁻¹	6.10±0.12	6	28.3±0.6	29.35±0.31	2.34±0.09	2.4±0.2	3560±120	NA
Nb (Low)	ng l ⁻¹	16±2	NA	23±3	NA	3.8±0.6	NA	< 0.8	NA
Nd (Low)	ng l ⁻¹	11±1	NA	375±6	NA	251±11	NA	10.2±0.2	NA
Ni (Medium)	µg l ⁻¹	59.7±0.4	60	27.9±1.3	27.4±0.8	0.709±0.051	0.67±0.08	0.57±0.03	0.709±0.054
P (Medium)	µg l ⁻¹	22.1±0.4	NA	7.3±1.7	NA	5.92±0.39	NA	33.6±2.4	NA
Pb (Low)	µg l ⁻¹	39.2±0.2	40	29.9±0.3	34.3±1.6	0.079±0.002	0.086±0.007	0.023±0.003	0.027±0.005
Pr (Low)	ng l ⁻¹	1.6±0.3	NA	95±5	NA	66±2	NA	2.5±0.4	NA
Rb (Low)	µg l ⁻¹	10.2±0.3	10	2.02±0.05	2.00±0.02	1.44±0.03	NA	28.8±0.9	NA
Re (Low)	ng l ⁻¹	< 0.5	NA	4.9±0.5	NA	6.5±0.2	NA	3.3±0.5	NA
S (Medium)	mg l ⁻¹	0.023±0.001	NA	3.34±0.06	NA	2.23±0.08	NA	240±12	NA
Sb (Low)	µg l ⁻¹	10.1±0.3	10	13.6±0.4	13.79±0.42	0.253±0.006	0.23±0.04	0.374±0.022	0.67*
Se (High)	µg l ⁻¹	9.63±0.44	10	20.5±0.9	21.96±0.51	< 0.050	NA	0.32±0.08	NA
Si (Medium)	mg l ⁻¹	0.028±0.002	NA	4.15±0.03	4.73±0.12	1.85±0.04	NA	0.29±0.03	NA
Sm (Low)	ng l ⁻¹	< 1	NA	62±2	NA	52±2	NA	7.8±0.2	NA
Sn (Low)	µg l ⁻¹	0.13±0.01	NA	1.47±0.04	NA	< 0.005	NA	< 0.020	NA
Sr (Low)	µg l ⁻¹	256±11	250	123±3	124.2±0.7	27.3±0.5	26.3±3.2	2000±60	NA
Ta (Low)	ng l ⁻¹	< 1	NA	6.8±0.3	NA	< 0.1	NA	< 0.4	NA
Tb (Low)	ng l ⁻¹	2.9±0.4	NA	8.8±0.2	NA	4.6±0.3	NA	0.9±0.2	NA
Te (Low)	µg l ⁻¹	3.37±0.09	3	0.051±0.020	NA	0.004±0.001	NA	0.031±0.004	NA
Th (Low)	ng l ⁻¹	2.9±0.7	NA	24±1	NA	17.5±0.6	NA	2.3±0.6	NA
Ti (Medium)	µg l ⁻¹	0.17±0.02	NA	0.44±0.7	NA	1.25±0.05	NA	0.051±0.009	NA
Tm (Low)	ng l ⁻¹	< 0.5	NA	1.8±0.2	NA	1.7±0.2	NA	< 0.2	NA
U (Low)	µg l ⁻¹	9.73±0.05	10	0.770±0.014	NA	0.047±0.001	0.050±0.003	0.97±0.03	1.2
V (Medium)	µg l ⁻¹	29.4±0.6	30	13.1±0.4	12.99±0.37	0.307±0.007	0.32±0.03	1.14±0.08	1.36*
W (Low)	ng l ⁻¹	24±3	NA	137±15	NA	< 0.5	NA	31±3	NA
Y (Low)	µg l ⁻¹	1.08±0.02	NA	0.164±0.002	NA	0.127±0.002	0.138*	0.028±0.002	NA
Yb (Low)	ng l ⁻¹	< 1	NA	10.1±2.7	NA	11.4±0.3	NA	1.2±0.4	NA
Zn (Medium)	µg l ⁻¹	72.7±1.2	70	54.5±0.4	53.2±1.1	1.07±0.04	0.93±0.10	0.97±0.16	1.10±0.14

NA – data not available

* - data from literature compilation

Table 1: Semi-quantitative results for water CRMs on the Thermo Scientific ELEMENT 2.

Conclusions

Sample screening using a semi-quantitative calibration in combination with internal standardization, provides a time-efficient and cost saving approach for the multi-elemental analysis of different sample types. Reasonably good accuracy can be obtained for the majority of analytes, provided that the instrument-specific response curve is properly adjusted. However, as has been shown from these results, the accuracy can potentially be affected for samples with heavy matrix. However, once such a problem is identified from this initial sample screening, the analytical approach for a subsequent high accuracy, fully quantitative analysis can be defined.

The Methods mentioned in this report can be downloaded from the Customer Information Service (CIS) section at www.thermo-bremen.com

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AN30005_E 08/16C